Microbial Production of Biofuels Using Lignocellulosic Waste Pretreated with Industrial Wastewater

Synopsis Submitted in The

Partial Fulfillment for The Requirement Of

Doctor Of Philosophy

In

Chemistry

Submitted by

Saurabh Kumar

Under the supervision of

Dr. Radhika Singh

Associate Professor

(Supervisor)

And

Dr. Yogita Jain

(Co-supervisor)

Department of Engineering

Department of Chemistry, Faculty of Science (Deemed University)

Dayalbagh Educational Institute

Dayalbagh, Agra-282005

2022

Introduction

From the beginning of the scientific era, all efforts have been made to understand the functioning of various natural laws and phenomena and to fulfill the energy demands of continuously increasing population. Energy is the central point of all scientific advancements (Edenhofer et al., 2015). As we are advancing day by day and our population is increasing, there is an increase in energy requirement. The increasing demand for energy along with the continuous increase in population leads to the energy crisis. The current situation is that about 1.4 billion people do not even have proper electricity supply. Due to lack of electricity, these people are dependent on the traditional sources of energy e.g., biomass burning, etc. which further contributes to air pollution (Kaygusuz, 2012).

Non – renewable resources: Major source of energy

Nonrenewable energy resources are those energy resources thatcannot be replenished naturally and have a limited supply. Currently, approximately 88% of energy comes out from non - renewable sources of energy e.g., fossil fuels such as petroleum, diesel, etc. (Nabi et al., 2009). Fossilfuels are available at lower costs because of the advanced technology therefore, we are highly dependent on these resources. The rate at which these non-renewable resources are depleting, our future generation may notbe able to use these resources (Chew et al., 2018). The excessive use of these traditional fuels will not only lead us to shortage of these limited renewable energy resources but also contribute to environmental pollutionsince fossil fuels emit various pollutants and greenhouse gases. At present time we are facing two interrelated problems globally - energy crisis and environmental pollution. To overcome these, we need some alternative green solutions so we can save non–renewable sources of energy for the future by reducing the dependence on these sources of energy (Kaygusuz, 2012).

Renewable energy sources: An alternative green solution

Renewable energy sources are those energy sources that replenish themselves naturally and would never deplete on the earth. Some examples of renewable sources of energy are bioenergy, hydropower, geothermal energy, solar energy, wind energy, and ocean (tide and wave) energy (Owusu & Asumadu, 2016). Renewable energy technologies have great potential to provide green energy and they reduce greenhouse gas emissions and global warmingby substituting fossil fuel-based conventional energy

sources (Panwar et al., 2011). Renewable energy sources supply approximately 29% of the world`s total energy demands which was not possible a decade ago (global energy review, 2021). The criteria for renewable energy are that it must be limitless in nature, and it should provide ecofriendly delivery of environmental goods and energy to be sustainable (Twidell & Weir, 2015). Renewable energy sources are obtained naturally from the energy that is flowing in the surroundings.

Biofuels are the future of renewable energy resources because they are eco-friendly, biodegradable, sustainable, and cost-effective. Biofuels are the promising alternative to fossil fuels (Bhattarai et al., 2011). There are various types of biofuels such as ethanol, hydrogen, methane, etc. Hydrogen as biofuel is a clean and high energyproducing fuel (122 MJ/Kg), which is three times higher than hydrocarbon fuel (Kapdan et al., 2006). On combustion H_2 produces water thus it does not contribute to the greenhouse gas effect. The heating value of $H_2$is about (61,100 Btu/Ib) and it is nearly three times of methane (23,879 Btu/Ib) (Bossel, 2003).

Classification of biofuel

Based on raw biomass sources, biofuels are divided into four generations (Alalwan et al.,2019).

First generation biofuels are those which are extracted from economically important and edible crops and biomass such as corn, sugarcane, rice, vegetables, etc. (Bhatia,2017). Although, a significant amount of biofuel can be extracted by various edible cropsand also the CO_2 emission can be reduced to about 80% (Jeihanipour, 2011). Production of biofuels from edible crops leads to food crisis (Paschalidou et al., 2016).

Second generation biofuels are those which come from non-edible biomass such as crop residue, litter, vegetable waste, fallen leaves, etc. utilization of such non-edible waste for biofuels production is an example of extraction of energy from waste. Second generation biofuels overcome the problem associated with first generation biofuels. Biofuelsfrom these biomassesare derived using various fermentation techniques (Hayeset al., 2015). The unique property of second-generation biofuel is that it is all about waste biomass and does not require cultivation, specific land type, water, etc. (Srivastava et al., 2019). Besides all these advantages method ofsecond-generation biofuel production is more expensive because these biofuels come mainly from lignocellulosic waste and extraction of

fermentable sugars from these wastes requires various chemical and physical pretreatments to eliminate or rupture the lignin binding (Bhatia, 2017).

Third generation biofuels are produced from aquatic weeds and algae. Seaweed produces unsaturated oil along with various biomolecules (Gambelli et al., 2017). Algae oil can be used to produce third generation fossil fuel and the main advantage is that there is no food versus fuel conflict since sea algae and weeds grow with a higher growth rate compared to terrestrial plantswhich do not require any special cultivation. But the disadvantage of the utilization of such photosynthetic algae is that the fuel generated from these is unstable because the oil produced from these is highly unsaturated. Also, the production of third generation biofuels is an expensive process (Shah et al., 2018).

Fourth generation biofuels are those which can be derived from genetically modified microorganisms such as microalgae, bacteria, etc. (Abdullahet al., 2019). Researchers are focusing on the method in which microalgae are genetically designed to consume more CO_2 and after cultivation, these will produce biofuels efficiently (Zhuet al., 2017). Generation of bioelectricity and biofuels is possible using advanced technology and some genetically modified bacteria.

Lignocellulosic waste biomass

Biofuels produced from lignocellulosic waste biomass are categorized as second-generation biofuels. These do not involve any edible or economically important crop biomass but utilizewaste from various agricultural crops and other lignocellulosic residues. According to (Ravindran et al., 2018) approximately five million tons of lignocellulosic waste are generated every year alone from the agricultural industry. Lignocellulose wastes also include timber, home, and garden waste. Lignocellulosic biomass can be broadly divided into four classes – grasses, hardwood, softwood, and farm waste (Chandel et al., 2018). Cellulose, hemicelluloses, and lignin are the three main components of Lignocellulosic biomass (Kumar and Sharma, 2017). Among these cellulose and hemicellulose are of main interest which can be utilized to generate biofuel using various techniques such as hydrolysis, anaerobic digestion, dark fermentation, etc., Among these components, lignin limits biofuel production. To overcome this limitation pretreatment of lignocellulosic waste is required in which the main aim is to rupture the lignin and expose cellulosic content (Kumari and Singh, 2018).

Fallen leaves: potential lignocellulosic waste

Fallen tree leaves arenatural renewable sources of energy and hence the potential source of biofuel production. The tree leaf contains a significant quantity of cellulose and hemicellulose approximately 13 to 25 percent and 15 to 25 percent respectively (Bakshi and Wadhwa, 2007). Another reason that makes it compatible to be a perfect second-generation biofuel producer is its availability and lack of any special cultivation. Every year in the autumn season tons of leaves fall from various species of trees of which only a small portion is utilized either as compost or burned directly (Springer, 2012). The burning of leaves is not beneficial either economically and environmentally. Fallen leaves burning emits various greenhouse gases which contribute to global warming (Razanov & Tkachuk, 2015). In a natural forest ecosystem, fallen leaves turn into humus by the natural decaying process and become nutrient sources for other plants and vegetation. In urban conditions, most of the tree leaves fall on roadsides, stones, concrete, etc. These cannot be turned into humus and become unwanted waste. Dumped fallen leaves emit methane which contribute to global warming. So, it would be good for the environment also if fallen leaves can be used as raw products for biofuel production (Muhammad & Chandra, 2021). Various lignocellulosic wastes have been investigated for biofuel production around the world and fallen leaves have a larger percentage of cellulosic material. Lignocellulosic content in various waste biomasses is given in table 1.

TABLE 1: Percent content in different lignocellulosic wastes.

Substrate	**Cellulose (%)**	**Hemicellulose (%)**	**Lignin (%)**	**Reference**
Fallen leaves	12.2 11.1	10.6 11.5	23.1 22.7	Liewetal., (2012) Liew etal., (2011)
Rice straw	44.3 29.2-34.7	34.5 23.0-25.9	20.4 17.0-19.0	Kumari& Singh, (2018) Cai etal., (2017)
Banana peels	60-65 41.38 11.45	6-8 9.90 25.52	5-10 8.90 9.82	Agustina and Susanti (2018) Kabenge et al., (2018) Orozco et al., (2014)
Water hyacinth	25 24.5 18.2	35 34.1 29.3	10 8.6 2.8	Bhattacharya& Kumar, (2010). Ruanet al., (2016) Ma et al., (2010)
Wheat straw	30 38.2 41-38	50 21.2 28-22	15 23.4 20-22	Kumari& Singh, (2018) Mosier etal., (2005) Huang etal., (2017)
Newspaper	40–55 49.3 48.5	25–40 12.2 9	18–30 19.18 23.9	Kumari & Singh, (2018) Guerfali et al., (2015) Barlaz, (2006)

Office paper	68.6 78.6 55.7	12.4 4.7 13	11.3 1.2 5.78	Mosier etal., (2005) Guerfaliet al., (2015) Barlaz, (2006)
Sugarcane bagasse	43-40 25-45	28-25 28-32	15-25 15-25	Zhou & Xu, (2019), Li etal., (2018) Cai etal., (2017)

Current uses of fallen leaves –

Currently, fallen leaves do not have any significant use. In natural forests, these leaves contribute to humic formation which has a significant role in soil fertility. But the fallen leaves in urban areas have limited uses.

- ✓ In most cases, fallen leaves are collected in bags and dumped to landfills where organic matter decomposes in anaerobic conditions and methanogenic bacteria degrades the organic matter to produce methane gas which contributes to global warming (U.S. Environmental Protection Agency, 2021).
- ✓ Another method of decomposition is the burning of collected dry leaves. This method can be considered as the worst kind of practice. Because fallen leaves have abundant carbon, burning of these causes air pollution.
- ✓ Some farmers use fallen leaves to make fertilizer for fields, but this process is timeconsuming also there are only a few farmers who use this method. This way of fallen leaves treatment is effective only if it is done on a large scale.

Petha wastewater

Scientific research is more beneficial ifit is problem orientated. Petha sweet is delicacy in the city of Tajmahal: Agra. In Agra, there are over 500 local Petha sweet manufacturing units (Singhal and Singh, 2015). It is made from Petha (*Benincasahispida).* Its making process involves soaking Petha overnight in lime water ($Ca(OH)_2$). After that lime water is discarded as such without any treatment and this wastewater flows into the Yamuna River causing water pollution. Lime water is highly alkaline in nature, and it is not good for aquatic river organisms. Therefore, PWW is the local problem in Agra city.

It is proposed to use highly alkaline PWW for pretreatment of fallen leaves. By utilizing PWW in the biofuel production process we can not only address the local problem but also forwarding a step towards green chemistry.

Proposed technique for biofuel production

For biofuel production using FL and PWW, anaerobic digestion will be used –

Anaerobic digestion

Anaerobic digestion is the process in which organic compound decays due to microbial activityin absence of oxygen and forms biogas. Biogas is composed of CH_4(50 to 70 %), CO_2 (50 to 30 %), mainlyand other gases as H_2S, etc. in trace amounts (Xu, 2017). Anaerobic digestion occurs in a series of steps that yield biogas. These steps are – (Gould, 2015)

a. **Hydrolysis -** is the first and important step of AD that makes it possible to utilize large polymers of an organic compound. In the hydrolysis step breakdown of large organic polymers of carbohydrates, proteins, and fats to their respective smaller units takes place.

$$(C_6H_{10}O_5)_n + nH_2O \rightarrow nC_6H_{12}O_6 + nH_2$$ (Anukam et al., 2019).

b. **Acidogenesis –** in this step acidogenic bacteria further breakdown the smaller units such as simple sugars, amino acids, and fatty acids. The acidic environment is created by producing volatile fatty acids, H_2, CO_2, H_2S, carbonic acids, alcohols, and other byproducts in trace amounts (Dang et al., 2016), (Bajpai, et al., 2017).

$$C_6H_{12}O_6 \leftrightarrow 2CH_3CH_2OH + 2CO_2$$

$$C_6H_{12}O_6 + 2H_2 \leftrightarrow 2CH_3CH_2COOH + 2H_2O$$

$$C_6H_{12}O_6 \rightarrow 3CH_3COOH$$

c. **Acetogenesis –**in this step acetogens produce acetate from products produced in the acidogenesis step. These bacteria produce CO_2, H_2, and acetic acid (Bajpai, et al., 2017).

$$CH_3CH_2COO^- + 3H_2O \leftrightarrow CH_3COO^- + H^+ + HCO_3^- + 3H_2$$

$$C_6H_{12}O_6 + 2H_2O \leftrightarrow 2CH_3COOH + 2CO_2 + 4H_2$$

$$CH_3CH_2OH + 2H_2O \leftrightarrow CH3COO^- + 3H_2 + H^+$$

d. **Methanogenesis –** it is the final step of AD in which methane is formed by acetates and hydrogen formed in the previous step (Anukam et al., 2019).

$$CO_2 + 4H_2 \longrightarrow CH_4 + 2H_2O$$

$$CH_3COOH \longrightarrow CH_4 + CO_2$$

From anaerobic digestion of biomassfew desirable biofuel outputs are as follows –

Biohydrogen –Lignocellulosic waste biohydrogen can be obtained through the AD process. The following reactions are involved (Osman et al., 2020)

$$2H_2 + 2e^- \rightarrow H_2$$

$$C_6H_{12}O_6 + 6H_2O \rightarrow 6CO_2 + 12H_2$$

$$C_6H_{12}O_6 + 2H_2O \rightarrow 2CH_3COOH + 2CO_2 + 4H_2$$

Bioethanol –is the intermediate compound in the AD process that is generated by microbial fermentation of organic compounds under anaerobic conditions. The reaction involved in ethanol production during fermentation is as follows - (Osman et al., 2020)

$$C_6H_{12}O_6 + 2H_2O \rightarrow C_2H_5OH + CH_3COOH + 2CO_2$$

Biomethanol – methane is the major product of AD, and it can be converted into methanol by methanotrophic bacteria in anaerobic conditions. The conversion takes place according to the following reaction - (Park and Lee, 2013)

$$CH_4 + 1/2O_2 \rightarrow CH_3OH$$

Brief Literature Survey

Burum (2008) characterized fallen tree leaves via classical characterization methods. Plant material contains a large amount of cellulose and other polysaccharides which are potential feedstocks for ethanol production.Results of this analysis demonstrated that the leaves were composed of cellulose (23.8 +/- 1.6%), xylan (7.4+/- 0.7%),arabinan (7.9+/-0.8%),acid-soluble lignin (22.3+/- 1.0%),acid-insoluble lignin (27.6%),and acid insoluble ash (2.6%).It was estimated that approximately 60 gallons of ethanol could be produced per ton of leaf litter.

Four lignocellulosic biomass feedstocks including corn stover, wheat straw, yard waste, and leaves were evaluated by **Liew etal. (2012)** for methane production via solid-state anaerobic digestion. Results showed that the highest methane yield was attained for corn stover (81.2 L kg^{-1} volatile solids (VS), followed by wheat straw (66.9 L kg^{-1}VS) leaves (55.4 L kg^{-1}VS) and yard waste (40.8 L kg^{-1} VS). This research paper suggests that leaves have low volatile solids (55.4 L kg^{-1}VS) compared to corn stover and wheat straw. Effluent from a mesophilic liquid AD system fed with municipal was used as inoculum in this research.

Comparison of pretreatment methods of fallen leaves for evaluation by Bio-ethanol raw material has been done by **Choi et al. (2014)**.In this study, fallen leaves are pretreated to produce bioethanol.Fallen leaves were treated with acid (HCl), alkali (NaOH, NH_3) and tested by applying the immersion method, stirring method, and autoclaving method.The treatment efficiency was confirmed by glucose production after enzymatic hydrolysis.It was found that alkaline pretreatment was 18% more effective than acidic pretreatment.Based on the results of this study, the feasibility of pre-treatment and enzymatic hydrolysis of fallen leaves, as the lignocellulosic substrate has been confirmed.

Anitha et al. (2015) investigated the potential of various animal and agricultural biomass including fallen leaves for methanol production. Methanol is the intermediate product that forms during the anaerobic digestion process. The study was carried out at room temperature and in the lab-scale reactor. Methanol formed during the anaerobic co-digestion process is characterized by the HPLC technique. Researchers have not carried out any chemical pretreatment before the AD process and used cow dung, goat dung, chicken manure as inoculum. Boiled rice (81.25 wt.%) and banana peels (61.51 wt.%) were found to have maximum bio-methanolyield while fallen leaves were found to have 16.02 wt.% methanol yield.

Nurmatov et al. (2016) in their research study produced solid fuel from leaf litter. They found that collection method and location affect the overall elemental properties. The researcher in this paper used various collection methods. They first washed the dry matter with a machine and then dehydrated it by mechanical pressing. Ash content was reduced by up to 60% with a washing treatment. According to their research study, the chemical composition of washed fallen leaves can be further improved if mechanical dehydration treatment is done which can eliminate the major portion of harmful elements for combustion such as K, Cl, Mg, and S.

The potential of fallen Teak (*Tectona grandis*) for biogas production was evaluated by **Wannapokin et al. (2017).** Fallen Teak leaves are composed of 48.88% C, 5.83% H, 0.55% N, 1.08% S and 30.04% O. Teak leaves contained 2.83% of moisture, 11.33% ash, 83.44% volatile matter, and 2.4% fixed carbon. Researchers estimated the theoretical yield of biogas and methane to be 1.074 m^3/kg and 0.5964 m^3 respectively. They concluded that fallen leaves biomass has great potential to produce biogas and methane and can be used as ferment substrates.

Lopez et al. (2021) reported a 30% increased production of ethanol and hydrogen by using an engineered *E. coli* strain. They used wheat straw and corn stover as the substrate for dark fermentation. For pretreatment, 1.5% dil. H_2SO_4 or 0.25% H_2SO_4 for autohydrolysis were used. The proposed biorefinery design contributed 20 – 30% of total ethanol production. The lignocellulosic biomass content for wheat straw was 48.88, 17.83, and 6.51%; and 43.00, 22.11, and 18.00% for corn straw, respectively.

The effect of Neem leaves litter on the composition of biogas produced from vegetable waste was studied by **Muhammad et al. (2021)**. Neem leaves litter is abundant in India. Besides its medicinal uses, there is no proper management for disposal. In this study Neem litter is anaerobically co-digested along with vegetable waste also compared the performance with results obtained from mono anaerobic digestion of vegetable waste and leaf litter of neem. Findings show that anaerobic co-digestion of vegetable waste and Neem litter leaves generated maximum biogas (87.27%) and methane (91.47%) and significantly reduced H_2S gas by 146.73%.

Objectives

Proposed objects are as follows -

- Pretreatment of fallen leaves collected from locally available tree species.
- To evaluate the effectiveness of pretreatment methods by analyzing pretreated biomass utilizing data generated from various techniques such as FESEM, FTIR, XRD, and others.
- To generate biofuels throughanaerobic digestionof fallen leaves.
- To optimize the efficiency of the ADreactorfor fallen leaves as substrate.
- Obtained results will be studied statistically with available statistical and mathematical tools like RSM.

Proposed Methodology

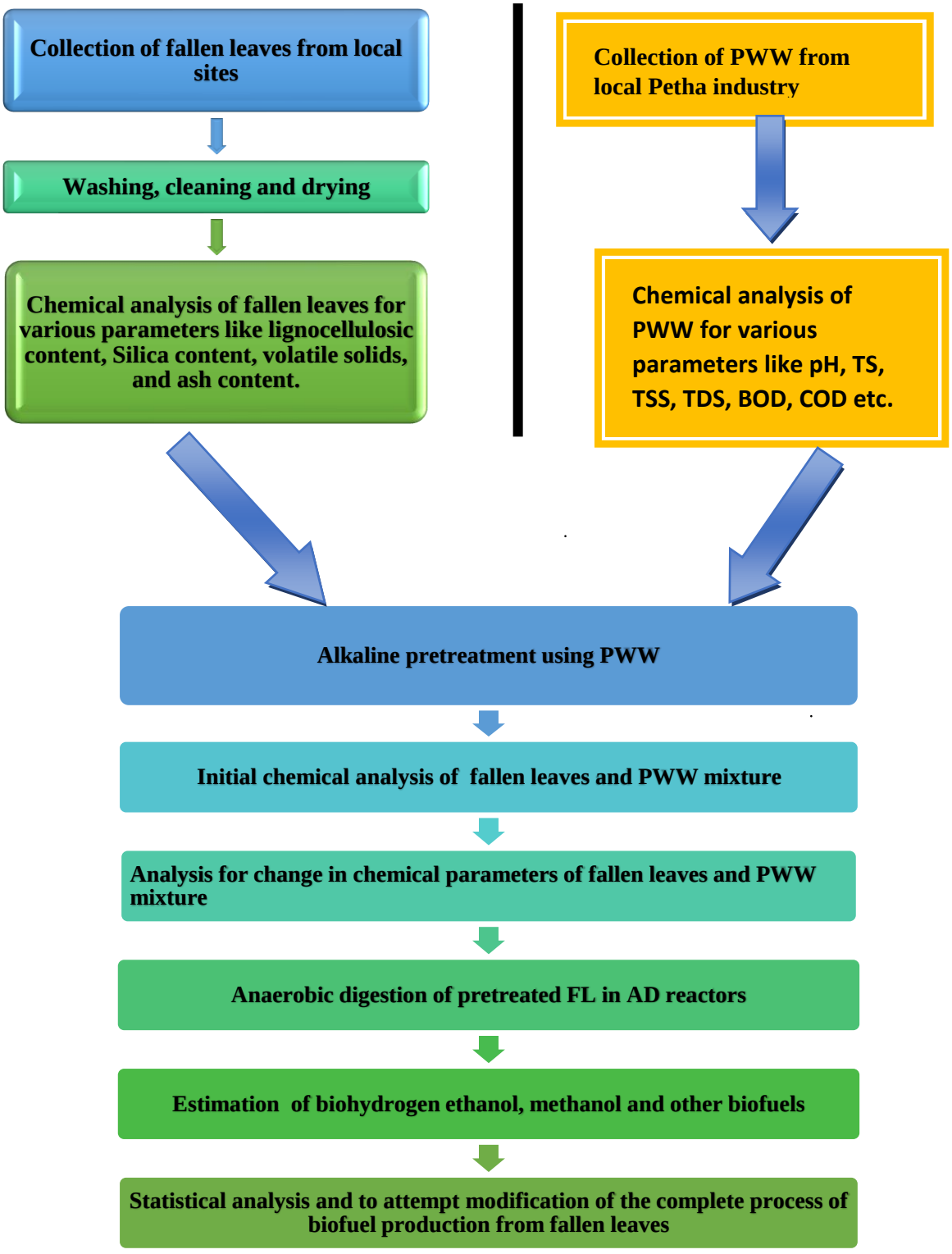
Collection of fallen leaves from local sites
Washing, cleaning and drying
Chemical analysis of fallen leaves for various parameters like lignocellulosic content, Silica content, volatile solids, and ash content.
Collection of PWW from local Petha industry
Chemical analysis of PWW for various parameters like pH, TS, TSS, TDS, BOD, COD etc.
Alkaline pretreatment using PWW
Initial chemical analysis of fallen leaves and PWW mixture
Analysis for change in chemical parameters of fallen leaves and PWW mixture
Anaerobic digestion of pretreated FL in AD reactors
Estimation of biohydrogen ethanol, methanol and other biofuels
Statistical analysis and to attempt modification of the complete process of biofuel production from fallen leaves

Fig. flowchart diagram of proposed methodology

References

Abdullah, B., Muhammad, S. A. F. A. S., Shokravi, Z., Ismail, S., Kassim, K. A., Mahmood, A. N., & Aziz, M. M. A. (2019). Fourth generation biofuel: A review on risks and mitigation strategies. *Renewable and sustainable energy reviews*, *107*, 37-50.

Agustina, E. W., & Susanti, V. E. (2018, May). Natural wrapping paper from banana (Musa paradisiaca Linn) peel waste with additive essential oils. In *Journal of Physics: Conference Series* (Vol. 1022, No. 1, p. 012032). IOP Publishing.

Alalwan, H. A., Alminshid, A. H., & Aljaafari, H. A. (2019). Promising evolution of biofuel generations. Subject review. *Renewable Energy Focus*, *28*, 127-139.

Anitha, M., Kamarudin, S. K., Shamsul, N. S., & Kofli, N. T. (2015). Determination of bio-methanol as intermediate product of anaerobic co-digestion in animal and agriculture wastes. *international journal of hydrogen energy*, *40*(35), 11791-11799.

Anukam, A., Mohammadi, A., Naqvi, M., & Granström, K. (2019). A review of the chemistry of anaerobic digestion: Methods of accelerating and optimizing process efficiency. *Processes*, *7*(8), 504.

Bajpai, P. (2017). Basics of anaerobic digestion process. In *Anaerobic Technology in Pulp and Paper Industry* (pp. 7-12). Springer, Singapore.

Bakshi, M. P. S., & Wadhwa, M. (2007). Tree leaves as complete feed for goat bucks. *Small Ruminant Research*, *69*(1-3), 74-78.

Barlaz, M. A. (2006). Forest products decomposition in municipal solid waste landfills. *Waste Management*, *26*(4), 321-333.

Bhatia, S. K., Kim, S. H., Yoon, J. J., & Yang, Y. H. (2017). Current status and strategies for second generation biofuel production using microbial systems. *Energy Conversion and Management*, *148*, 1142-1156.

Bhattacharya, A., & Kumar, P. (2010). Water hyacinth as a potential biofuel crop. *Electron J Environ Agric Food Chem*, *9*(1), 112-122.

Bhattarai, K., Stalick, W. M., Mckay, S., Geme, G., & Bhattarai, N. (2011). Biofuel: an alternative to fossil fuel for alleviating world energy and economic crises. *Journal of Environmental Science and Health, Part A*, *46*(12), 1424-1442.

Bossel, U. (2003, October). Well-to-wheel studies, heating values, and the energy conservation principle. Technical report, European Fuel Cell Forum, Morgenacherstrasse.

Burum, J. (2008). Characterization of Fall Leaves as a Source of Cellulosic Ethanol. *Journal of Undergraduate Research at Minnesota State University, Mankato*, *8*(1), 2.

Cai, J., He, Y., Yu, X., Banks, S. W., Yang, Y., Zhang, X., & Bridgwater, A. V. (2017). Review of physicochemical properties and analytical characterization of lignocellulosic biomass. *Renewable and Sustainable Energy Reviews*, *76*, 309-322.

Chandel, A. K., Garlapati, V. K., Singh, A. K., Antunes, F. A. F., & da Silva, S. S. (2018). The path forward for lignocellulose biorefineries: bottlenecks, solutions, and perspective on commercialization. *Bioresource technology*, *264*, 370-381.

Chew, K. W., Chia, S. R., Show, P. L., Yap, Y. J., Ling, T. C., & Chang, J. S. (2018). Effects of water culture medium, cultivation systems and growth modes for microalgae cultivation: a review. *Journal of the Taiwan Institute of Chemical Engineers*, *91*, 332-344.

Choi, H., Kim, J., & Pak, D. (2014). Comparison of pretreatment of fallen leaves for application evaluation by bio-ethanol raw material. *Journal of Energy Engineering*, *23*(3), 241-246.

Dang, Y., Holmes, D. E., Zhao, Z., Woodard, T. L., Zhang, Y., Sun, D., & Lovley, D. R. (2016). Enhancing anaerobic digestion of complex organic waste with carbon-based conductive materials. *Bioresource technology*, *220*, 516-522.

Edenhofer, O. (Ed.). (2015). *Climate change 2014: mitigation of climate change* (Vol. 3). Cambridge University Press.

Gambelli, D., Alberti, F., Solfanelli, F., Vairo, D., & Zanoli, R. (2017). Third generation algae biofuels in Italy by 2030: A scenario analysis using Bayesian networks. *Energy Policy*, *103*, 165-178.

Gould, M. C. (2015, January). Bioenergy and anaerobic digestion. In *Bioenergy* (pp. 297-317). Academic Press.

Guerfali, M., Saidi, A., Gargouri, A., & Belghith, H. (2015). Enhanced enzymatic hydrolysis of waste paper for ethanol production using separate saccharification and fermentation. *Applied biochemistry and biotechnology*, *175*(1), 25-42.

Hayes, C. J., Burgess Jr, D. R., & Manion, J. A. (2015). Combustion pathways of biofuel model compounds: A review of recent research and current challenges pertaining to first-, second-, and third-generation biofuels. *Advances in Physical Organic Chemistry*, *49*, 103-187.

https://www.epa.gov/ (U.S. Environmental Protection Agency, 2021). Accessed on 15/10/2021

Huang, C., Lai, C., Wu, X., Huang, Y., He, J., Huang, C., & Yong, Q. (2017). An integrated process to produce bio-ethanol and xylooligosaccharides rich in xylobiose and xylotriose from high ash content waste wheat straw. *Bioresource technology*, *241*, 228-235.

IEA (2021), Global Energy Review 2021, IEA, Paris https://www.iea.org/reports/global-energy-review-2021. (Accessed on 25/10/2021)

Jeihanipour, A. (2011). *Waste textiles bioprocessing to ethanol and biogas* (Doctoral dissertation, Chalmers University of Technology).

Kabenge, I., Omulo, G., Banadda, N., Seay, J., Zziwa, A., & Kiggundu, N. (2018). Characterization of banana peels wastes as potential slow pyrolysis feedstock. *Journal of Sustainable Development*, *11*(2), 14-24.

Kapdan, I. K., & Kargi, F. (2006). Bio-hydrogen production from waste materials. *Enzyme and microbial technology*, *38*(5), 569-582.

Kaygusuz, K. (2012). Energy for sustainable development: A case of developing countries. *Renewable and Sustainable Energy Reviews*, *16*(2), 1116-1126.

Kumar, A. K., and Sharma, S. (2017). Recent updates on different methods of pretreatment of lignocellulosic feedstocks: a review. *Bioresour. Bioprocess* 4:7. doi: 10.1186/s40643-017-0137-9.

Kumari, D., & Singh, R. (2018). Pretreatment of lignocellulosic wastes for biofuel production: a critical review. *Renewable and Sustainable Energy Reviews*, *90*, 877-891.

Li, H., Chen, X., Xiong, L., Luo, M., Chen, X., Wang, C., & Chen, X. (2019). Stepwise enzymatic hydrolysis of alkaline oxidation treated sugarcane bagasse for the co-production of functional xylo-oligosaccharides and fermentable sugars. *Bioresource technology*, *275*, 345-351.

Liew, L. N., Shi, J., & Li, Y. (2011). Enhancing the solid-state anaerobic digestion of fallen leaves through simultaneous alkaline treatment. *Bioresource technology*, *102*(19), 8828-8834.

Liew, L. N., Shi, J., & Li, Y. (2012). Methane production from solid-state anaerobic digestion of lignocellulosic biomass. *Biomass and Bioenergy*, *46*, 125-132.

Lopez-Hidalgo, A. M., Magaña, G., Rodriguez, F., De Leon-Rodriguez, A., & Sanchez, A. (2021). Co-production of ethanol-hydrogen by genetically engineered Escherichia coli in sustainable biorefineries for lignocellulosic ethanol production. *Chemical Engineering Journal*, *406*, 126829.

Ma, F., Yang, N., Xu, C., Yu, H., Wu, J., & Zhang, X. (2010). Combination of biological pretreatment with mild acid pretreatment for enzymatic hydrolysis and ethanol production from water hyacinth. *Bioresource technology*, *101*(24), 9600-9604.

Mosier, N., Wyman, C., Dale, B., Elander, R., Lee, Y. Y., Holtzapple, M., & Ladisch, M. (2005). Features of promising technologies for pretreatment of lignocellulosic biomass. *Bioresource technology*, *96*(6), 673-686.

Muhammad, M. B., & Chandra, R. (2021). Enhancing biogas and methane production from leaf litter of neem by co-digestion with vegetable waste: Focus on the effect of tannin. *Biomass and Bioenergy*, *147*, 106007.

Nabi, M. N., Hoque, S. N., & Akhter, M. S. (2009). Karanja (Pongamia Pinnata) biodiesel production in Bangladesh, characterization of karanja biodiesel and its effect on diesel emissions. *Fuel processing technology*, *90*(9), 1080-1086.

Nurmatov, N., Leon Gomez, D. A., Hensgen, F., Bühle, L., & Wachendorf, M. (2016). High-quality solid fuel production from leaf litter of urban street trees. *Sustainability*, *8*(12), 1249.

Orozco, R. S., Hernández, P. B., Morales, G. R., Núñez, F. U., Villafuerte, J. O., Lugo, V. L., & Vázquez, P. C. (2014). Characterization of lignocellulosic fruit waste as an alternative feedstock for bioethanol production. *BioResources*, *9*(2), 1873-1885.

Osman, Ahmed I.; Deka, Tanmay J.; Baruah, Debendra C.; Rooney, David W. (2020). *Critical challenges in biohydrogen production processes from the organic feedstocks. Biomass Conversion and Biorefinery*, doi:10.1007/s13399-020-00965-x.

Owusu, P. A., &Asumadu-Sarkodie, S. (2016). A review of renewable energy sources, sustainability issues and climate change mitigation. *Cogent Engineering*, *3*(1), 1167990.

Panwar, N. L., Kaushik, S. C., & Kothari, S. (2011). Role of renewable energy sources in environmental protection: A review. *Renewable and sustainable energy reviews*, *15*(3), 1513-1524.

Park, D., & Lee, J. (2013). Biological conversion of methane to methanol. *Korean Journal of Chemical Engineering*, *30*(5), 977-987.

Paschalidou, A., Tsatiris, M., & Kitikidou, K. (2016). Energy crops for biofuel production or for food SWOT analysis (case study: Greece). *Renewable Energy*, *93*, 636-647.

Ravindran, R., et al. (2018). A review on bioconversion of agro-industrial wastes to industrially important enzymes. *Bioengineering*, *5*(4), 93.

Razanov, S., & Tkachuk, O. (2015). Porivnyalniy analizvikidiv zabrudnyuyuchihrechovin u povitrya traditsiynimi energonosiyami ta riznimi vidami biopaliva [The comparative analysis of pollutant emissions is into the air by traditional energy and different types of biofuels]. *Silske gospodarstvo ta lisivnitstvo*, *1*, 152-160.

Ruan, T., Zeng, R., Yin, X. Y., Zhang, S. X., & Yang, Z. H. (2016). Water hyacinth (Eichhornia crassipes) biomass as a biofuel feedstock by enzymatic hydrolysis. *BioResources*, *11*(1), 2372-2380.

Shah, S. H., Raja, I. A., Rizwan, M., Rashid, N., Mahmood, Q., Shah, F. A., & Pervez, A. (2018). Potential of microalgal biodiesel production and its sustainability perspectives in Pakistan. *Renewable and Sustainable Energy Reviews*, *81*, 76-92.

Singhal, Y., & Singh, R. (2015). Energy recovery from petha industrial wastewater by anaerobic digestion. *Int J Sci Eng*, *2*(3), 146-151.

Springer, T. L. (2012). Biomass yield from an urban landscape. *Biomass and Bioenergy*, *37*, 82-87.

Srivastava, N., Kharwar, R. K., & Mishra, P. K. (2019). Cost economy analysis of biomass-based biofuel production. In *New and Future Developments in Microbial Biotechnology and Bioengineering* (pp. 1-10). Elsevier.

Twidell, J., & Weir, T. (2015). *Renewable energy resources*. Routledge.

Wannapokin, A., Ramaraj, R., & Unpaprom, Y. (2017). An investigation of biogas production potential from fallen teak leaves (Tectona grandis). *Emergent Life Sciences Research*, *3*, 1-10.

Xu, F. (2017). *Encyclopedia of Sustainable Technologies, Biomass Digestion. 197–204.* doi:10.1016/B978-0-12-409548-9.10108-3.

Zhou, X., & Xu, Y. (2019). Integrative process for sugarcane bagasse biorefinery to co-produce xylooligosaccharides and gluconic acid. *Bioresource technology*, *282*, 81-87.

Zhu, B., Chen, G., Cao, X., & Wei, D. (2017). Molecular characterization of CO2 sequestration and assimilation in microalgae and its biotechnological applications. *Bioresource technology*, *244*, 1207-1215.